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Unique Hydride Chemistry on Silicon - PH_3 Interaction with Si(100)-(2x1)

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Abstract

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Abstract

The dissociative adsorption of phosphine (PH$_3$) on Si(100)-(2x1) and its high temperature thermal behavior have been studied by high-resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES) and by temperature programmed desorption (TPD). Phosphine adsorbs dissociatively onto Si(100)-(2x1) at 100 K as PH$_2$ and H species, as revealed by vibrational bands at 1050 cm^{-1} [δ_{sc} (PH$_2$)] and 2100 cm^{-1} [ν(Si-H)]. The PH$_2$(a) undergoes thermal decomposition to adsorbed P and H near 650 K, as determined by HREELS. TPD measurements reveal two PH$_3$ desorption processes at 485 and 635 K. The 635 K-desorption is shown to result from PH$_2$ + H recombination, while the mechanism for the 485 K-desorption cannot be definitively identified. Additionally, two H$_2$ desorption states were observed at 685 and 770 K. Comparison of these features with H$_2$ desorption from clean and phosphorus-modified silicon indicates that the 685- and 770 K-H$_2$ desorption kinetics are controlled by thermal dissociation of adsorbed PH$_x$ species which supply hydrogen to the surface.

2

I. Introduction

The chemical vapor deposition of doped semiconductor films is typically accomplished at an interface by the thermal decomposition of small hydride molecules which are utilized due to their high vapor pressures and chemical simplicity [1]. Two examples are silane (SiH_4), which is used to deposit elemental silicon, and diborane (B_2H_6), which is used to deliver boron to the growing film.

Another very important dopant utilized in the semiconductor industry is phosphorus. The incorporation of phosphorus into silicon films is often achieved by phosphine (PH_3) adsorption onto freshly deposited silicon films, followed by desorption of the co-adsorbed hydrogen atoms. This apparently simple process of adsorbing phosphine and desorbing H_2 has been studied by a variety of surface sensitive techniques over the past 25 years. While progress has been made, several fundamental questions have yet to be resolved; these concern the surface species which form upon phosphine exposure to silicon, and the thermal stability of these species.

Early studies used low energy electron diffraction (LEED) to examine the surface structures which resulted after phosphine exposure to a Si(111)-(7x7) surface at temperatures between 300 - 773 K [2,3]. While several complex ordered LEED structures were observed, their corresponding surface structure could not be determined.

Recent studies have examined the reactivity of phosphine with the structurally simpler Si(100)-(2x1) surface. Phosphine was found to have an initial sticking coefficient of unity on the Si(100)-(2x1) surface at 300 K and to saturate after exposures of 3 - 5 Langmuir [4]. This saturation phosphorus coverage was found to increase upon PH_3 exposures at higher substrate temperatures [5].

3

The nature of the PH$_3$-Si bonding was first addressed by Yu et al. in 1986 [6]. The authors reported that on the Si(100)-(2x1) surface phosphine "mostly adsorbs non-dissociatively" at 300 K, while molecular and dissociative adsorption was reported upon adsorption at 575 K. This molecularly bound phosphine was postulated to utilize the phosphorus lone-pair to form a bridge bond across a silicon dimer [6]. Heating to ~775 K caused the desorption of H$_2$, and at a temperature of ~825 K P$_2$ was liberated from the surface [6].

A different model for phosphine adsorption on Si(111)-(7x7) was proposed by Taylor et al. [7] and Wallace et al. [8]. Utilizing Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), temperature programmed desorption (TPD) and electron stimulated decomposition (ESD), these authors reported that phosphine adsorbed dissociatively on the Si(111)-(7x7) surface at 120 K [7,8] with a sticking coefficient of unity up to 75% of saturation coverage. Their TPD studies yielded H$_2$ and P$_2$ desorption processes at 740 and 1010 K, respectively. A recent HREEL study confirmed the dissociation of PH$_3$ on the Si(111)-(7x7) surface at 120 K, and also assigned a P-H vibration at 1050 cm^{-1} to the -PH$_2$ scissor mode [9]. This was the first direct experimental evidence that -PH$_2$ species formed from PH$_3$ on the Si(111)-(7x7) surface upon adsorption at 120 K. Complete decomposition of the PH$_2$(a) to P(a) + 2H(a) was observed upon heating to 500 K [9].

In this study we examine the bonding and high temperature behavior of phosphine on the Si(100)-(2x1) crystal face. Phosphine dissociatively adsorbs on Si(100)-(2x1), leaving PH$_2$(a) and H(a) species on the surface. Unlike the thermal behavior on Si(111)-(7x7) [7-10], PH$_2$(a) + H(a) recombine on the Si(100)-(2x1) surface to liberate PH$_3$(g) at 635 K. We also observe two H$_2$ desorption states from the PH$_3$/Si(100)-(2x1) interface, at 685 and 770 K. Thermal desorption studies from co-adsorbed phosphorus and hydrogen, which yield different

4

desorption kinetics, lead us to propose that P-H bond rupture from adsorbed PH_x species controls the desorption kinetics of H_2.

II. Experimental

The experiments reported in this work were performed in a stainless-steel ultra high vacuum (UHV) chamber which has been described previously [11]. Briefly, vibrational spectroscopic studies were carried out in a Leybold-Heraeus ELS-22 high-resolution electron energy loss spectrometer (HREELS) utilizing a 4.2 eV primary excitation beam. The elastic beam measured ~1 x 10^5 counts per second (cps) from the clean surface and ~5 x 10^4 cps from the PH_3 covered silicon surface. The beam typically had a full width at half maximum (FWHM) of 65 - 70 cm^{-1}. All HREEL data were recorded by a multichannel analyzer and were smoothed following data acquisition using a simulated RC filtering program which is described in a previous publication [12].

Temperature programmed desorption (TPD) experiments were performed with a UTI 100C quadrupole mass spectrometer (QMS) mounted behind a 3 mm diameter aperture. The data were accumulated in a Teknivent multiplexer, which allowed the simultaneous recording of up to six desorbing species. All TPD data shown are in raw data form; no smoothing routines have been employed.

The Si(100) crystal (5-10 Ω-cm, B-doped, 13 x 13 x 1.5 mm) was fastened between two electrically isolated tungsten leads (1 mm diameter) by two pieces of thin tantalum foil. Each piece of foil was wrapped around a tungsten lead and wedged into one of two pre-cut slots (0.38 mm width) on opposite edges of the crystal. This mounting scheme allowed the crystal to be heated to 1400 K by simply passing current through the tungsten/foil/crystal assembly. To achieve a linear heating rate, a Honeywell Universal Digital 5000 Ultra-Pro Controller was used to regulate the power output from a direct current power supply (maximum

5

current = 50 A; maximum voltage = 100 V). Cooling the crystal was accomplished by direct thermal contact of the mounting assembly to a liquid-N_2 cooled resevoir in the manipulator.

The Si(100) crystal was subjected to a chemical cleaning procedure prior to its insertion into vacuum. The procedure utilized hydrogen peroxide to oxidize the contaminated overlayer of the crystal surface, and employed an aqueous HF solution (49%) to strip-off the contaminated oxide [13]. This procedure was found to remove any metal contamination which resulted from the cutting of slots into the sides of the crystal [14]. No evidence in the Auger spectra was found for nickel or any other metal contamination in the silicon crystal after heating in vacuo.

After insertion of the Si(100) crystal into the vacuum chamber and baking to 150 °C for two days, the crystal surface was found to be contaminated with carbon and oxygen. Flashing to 1100 K sufficed to remove the oxide layer; however, removal of the carbon contamination required repeated Ar^+ ion sputtering (2.5 keV). To regenerate a (2x1) surface structure after sputtering, the crystal was annealed to 1150 K and then cooled to 100 K in approximately 15 minutes. This produced a Si(100) crystal with a well-ordered (2x1) structure, as determined by low energy electron diffraction (LEED), and a carbon concentration below 0.5 atom % in the depth of Auger sampling.

The PH_3 gas used in this study was purchased from Matheson Gas Products (99.9% pure) and transferred to a stainless-steel cylinder after several freeze-pump-thaw cycles. The gas was introduced onto the Si(100)-(2x1) surface through a stainless-steel gas handling system which was attached to a translatable micro-capillary array doser containing an internal 2μ pinhole. A similar system has been described in detail previously [15]. The flux of the PH_3 at the crystal surface was calculated using the PH_3 effusion rate through our doser, corrected with a

6

geometrical factor (0.50) which was based on our doser-sample geometry [16,17]. To check the accuracy of this method, the adsorption of PH_3 was measured kinetically by using the QMS to monitor the PH_3 pressure during adsorption with the crystal in the molecular beam. The saturation coverage (PH_3 molecules/cm^2) was found to be within 8% of the full coverage measured in a previous study [7].

III. Results and Discussion

A. HREEL Study of the PH_3/Si(100)-(2x1) Interface

Figure 1(a) proves that even at 100 K, phosphine adsorbs dissociatively on the Si(100)-(2x1) surface. The appearance of a Si-H stretching mode at 2100 cm^{-1} [18], the P-H stretching mode at 2300 cm^{-1} [19] and the Si-P stretching mode at 495 cm^{-1} [9] confirms that the PH_3 has reacted with the silicon surface to produce adsorbed PH_x ($3 \geq x \geq 1$) and H species. Addition information is obtained from the feature observed at 1050 cm^{-1} [Fig. 1(a)], which a previous vibrational study of PH_3 on Si(111)-(7x7) has assigned to a PH_2 scissor mode [9]. This assignment was based on the similarity between the 1050 cm^{-1} loss and the vibrational frequencies from seven compounds which contained the -PH_2 moiety [9]. Therefore, based on the 2100 cm^{-1} [v(Si-H)] mode and the 1050 cm^{-1} [$\delta_{sc}(PH_2)$] mode, it follows that PH_2(a) and H(a) species are produced by phosphine adsorption on Si(100)-(2x1) at 100 K. The only other vibrational loss appears at 640 cm^{-1}, and is assigned to a Si-H bending mode [18]. All these spectral assignments are supported by the results of our heating experiments.

Heating the PH_3/Si(100)-(2x1) layer between 100 and 500 K does not produce any significant changes in the adsorbed layer, as judged by the vibrational spectra [Fig. 1(a-c)]. However, heating to a temperature of 600 K causes the onset of PH_2(a) dissociation. This is observed clearly from the intensity attenuations of the PH_2 scissor mode intensity at 1050 cm^{-1} and the P-H stretching mode at 2300

cm^{-1} [Fig. 1(d)]. The P-H vibrational modes decrease in intensity while increases in the Si-H stretching and bending mode intensities are observed at 2120 and 640 cm^{-1}, respectively. Continued heating to 650 K for one minute [Fig. 1(e)] removes fully the PH$_2$ scissor mode intensity at 1050 cm^{-1} and the P-H stretching mode intensity at 2300 cm^{-1}. This leaves a vibrational spectrum devoid of any P-H related species. Only Si-H modes (640 and 2120 cm^{-1}) and the Si-P modes (465 and 900 cm^{-1}) remain. Heating to 900 K causes the additional removal of all Si-H related vibrations [Figs. 1(g)]. The development of vibrational features at ~400 and ~900 cm^{-1} is indicative of silicon-phosphide formation. These features have also been observed after PH$_3$ exposures on Si(111)-(7x7), followed by heating to 900 K [9].

Our studies also utilized HREELS to study initial PH$_3$ exposures as high as 1.3×10^{15}/cm^2 onto Si(100)-(2x1) at 100 K. The spectra are not shown since they were nearly identical at all temperatures to the vibrational spectra recorded after a 1×10^{14} PH$_3$/cm^2 exposure, shown in Fig. 1.

Summarizing our HREEL results, we have shown that PH$_3$ dissociatively adsorbs onto Si(100)-(2x1) as PH$_2$(a) and H(a) at 100 K. The PH$_2$ species decompose after heating to 650 K for one minute, leaving adsorbed P and H. Heating to 900 K causes the removal of all Si-H vibrational modes.

B. Temperature Programmed Desorption Results

1. Phosphine Desorption Kinetics

Temperature programmed desorption studies after PH$_3$ exposures onto Si(100)-(2x1) reveal very interesting results for the H$_2$ and the PH$_3$ desorbing species. First we shall examine the desorption of molecular phosphine from the surface. As shown in Fig. 2A(a), a low exposure of 5×10^{13} PH$_3$/cm^2 on Si(100)-(2x1) does not lead to desorption of any PH$_3$ between 100 - 1000 K. A

8

phosphine exposure of $1 \times 10^{14}/cm^2$, however, produces two molecular phosphine desorption peaks at 485 and 635 K [Fig. 2A(b)]. These desorption features increase in intensity with higher initial PH_3 exposures [Fig. 2A(b-d)]. Isotopic exchange studies show definitively that the 635 K peak is due to $PH_2(a) + H(a)$ recombinative desorption (to be discussed). The mechanism for the 485 K PH_3 desorption is uncertain.

After an exposure of ~2×10^{14} PH_3/cm^2, a very broad lower-temperature (200 - 400 K) PH_3 desorption feature develops which increases in intensity after higher PH_3 exposures [Figs. 2A(c-d)]. However, results from a TPD experiment which did not involve line-of sight mass spectrometer detection geometry indicated that this broad desorption feature is at least partly caused by desorption of PH_3 from the crystal support assembly. Also while TPD studies showed this feature to increase at higher initial exposures, both AES and HREELS did not show any spectral changes upon continued exposure. Therefore, since it is likely that this feature is not entirely associated w   Jsorption on the Si(100) crystal, we shall not consider it further.

2. Hydrogen Desorption Kinetics

Figure 2(B) shows the desorption of molecular hydrogen from a $PH_3/Si(100)$-(2x1) interface as a function of PH_3 exposure. A low phosphine exposure of $5 \times 10^{13}/cm^2$ [Fig. 2B(a)] produces only one H_2 desorption feature at 770 K. Similar desorption features have been reported for a variety of H-containing adsorbates on Si [7,8,10,20-23]. However, at higher PH_3 exposures, two hydrogen desorption features are observed at 685 K and 770 K.

Four hydrogen desorption experiments are shown in Figure 3. Figure 3A shows the two desorption states of hydrogen originating from PH_3. Figure 3B shows the hydrogen desorption from pure atomic hydrogen adsorption on Si(100)-(2x1); major desorption processes at 740 K and 640 K are observed as well as a

9

broad low-intensity hydrogen evolution process centered at about 360 K, in agreement with other H·/Si experiments [18,24]. A comparison of Figure 3A with Figure 3B shows that the desorption kinetics differ for hydrogen from PH_3 adsorption compared to hydrogen from a fully hydrogen-covered surface. Hydrogen desorption occurs at higher temperatures from layers produced from PH_3 compared to layers produced by pure atomic hydrogen adsorption.

In order to determine whether the presence of atomic P(a) on Si(100) significantly influences hydrogen desorption kinetics, two additional experiments were performed and are shown in Figures 3C and 3D. Here, surface P(a) is generated by decomposition of PH_3 at 900 K, and then atomic hydrogen is adsorbed to two levels of coverage [25]. The P(a) coverage is estimated to be 0.25 ML based on the initial PH_3 exposure at 90 K and the small P_2 desorption (~ 5%) as detected by TPD. The hydrogen desorption kinetics from the phosphorus-covered surface, as indicated by the three states at 360 K, 640 K and 740 K, closely resemble the desorption kinetics obtained from pure hydrogen layers [18,24]; adsorbed phosphorus has little or no effect on the hydrogen desorption kinetics.

Thus the experiments in Figure 3 suggest that H_2 desorption from layers produced by PH_2 decomposition is retarded slightly compared to H_2 desorption from pure hydrogen layers or from phosphorus modified layers. The increased temperature of the H_2 desorption features from PH_3-derived layers is attributed to the involvement of P-H bond scission in the remaining $PH_2(a)$ or PH(a) species; the P-H bond breaking supplies hydrogen to the surface in a rate-controlling manner for a portion of the hydrogen which is desorbed. Comparison with HREELS measurements indicates that we cannot determine whether the decomposition of $PH_2(a)$ or PH(a) controls the H_2 desorption kinetics.

3. Desorption of Other Species from PH$_3$ Treated Si(100)

Line-of-sight thermal desorption experiments were used to look for other species, such as P$_2$ (mass 62) and P$_2$H$_4$ (major mass spectrometer cracking product at mass 64 [26]). P$_2$ was observed to desorb with a peak temperature of 945 K; in comparison, P$_2$ desorbs at 1010 K from a Si(111) surface following PH$_3$ adsorption [8,9]. P$_2$H$_4$ desorption was not observed from Si(100).

C. Isotopic Exchange Studies

Figure 4 shows an experiment in which PH$_3$ was adsorbed on a Si(100) surface partially covered with D(a) species. Both PH$_3$ and PH$_2$D are observed at 635 K, indicating that the 635 K phosphine desorption process occurs by means of a recombination step between PH$_2$(a) and H(a) or D(a). This result is similar to that obtained for NH$_2$ on Si(100), where a high temperature recombination process to produce NH$_3$ was also observed [10,22,27,28]. HREELS studies of a mixed D(a) and PH$_x$(a) layer did not disclose a P-D stretching mode (1625 cm^{-1}) within the detection limit of HREELS.

Figure 5 involves a study of the hydrogen isotopes desorbing from a layer produced by PH$_3$ adsorption on a partially covered D(a) layer. The hydrogen isotopic species HD and D$_2$ are observed to be liberated above 600 K. This is consistent with two models:

(1) P-H bond scission is rate controlling in HD desorption from surfaces containing D(a).

(2) P-H bonds exchange with D(a) to produce P-D bonds in PH$_x$(a) species.

11

IV. Summary

We have used HREELS and TPD to study the adsorption and decomposition of PH_3 on Si(100)-(2x1) surfaces in the temperature range 100 K to 1000 K. The following results have been obtained:

1. PH_3 dissociatively adsorbs on Si(100)-(2x1) at 100 K producing $PH_2(a)$ and H(a).

2. The $PH_2(a)$ species are thermally stable up to about 600 K, where additional P-H bond scission occurs.

3. No evidence for the existence of PH(a) species was obtained by vibrational spectroscopy.

4. A recombination process involving $PH_2(a)$ and H(a) was observed at 635 K, producing $PH_3(g)$.

5. Evidence for HD(g) production from $PH_2(a)$ and D(a) was obtained at temperatures above 600 K.

6. Kinetic studies of hydrogen desorption from $PH_x(a)$ species indicate that P-H bond scission is involved in controlling the kinetics of hydrogen desorption. This hydrogen desorption from layers produced from PH_3 is compared to layers produced from pure atomic hydrogen adsorption. An alternate model in which adsorbed P influences the kinetics of H_2 desorption is not supported by coadsorption experiments involving P(a) and H(a).

V. Acknowledgment

Figure Captions

Figure 1. HREEL spectra showing the effects of heating on a low coverage of PH_3 on Si(100)-(2x1). All spectra were recorded at 90 K after heating to the indicated temperature for one minute.

Figure 2. TPD spectra of PH_3 and H_2 from PH_3/Si(100)-2x1) interfaces at various coverages. The heating rate was 2 K/s.

Figure 3. TPD spectra (dT/dt = 2 K/s) monitoring the release of H_2 from clean and phosphorus-modified Si(100)-(2x1); (A) a PH_3/Si(100)-(2x1) interface; (B) dihydride species on a Si(100)-(2x1) surface; (C) dihydride species on the Si(100)-(2x1) surface which had been dosed with PH_3 and heated to 900 K; (D) a layer similar to (C), but containing only monohydride species [25].

Figure 4. TPD spectra (dT/dt = 2 K/s) of PH_3 and PH_2D desorption from a deuterium pre-capped (Θ_D = 0.12 ML) surface after an exposure of 2 x 10^{14} PH_3/cm^2 at 100 K. The PH_2D species observed at 635 K shows a recombinative PH_2(a) + H(a) process is occurring on the surface.

Figure 5. TPD spectra (dT/dt = 2 K/s) of (a) H_2, (b) HD and (c) D_2 desorption from a deuterium pre-capped surface exposed to PH_3 at 100 K. Both desorption features are evident in all three desorbing species.

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25. The H-exposures were chosen to ensure dihydride [Fig. 3(C)] and monohydride [Fig. 3(D)] species on the phosphorus-modified silicon. The presence (and absence) of dihydride species was confirmed by the intense 925 cm^{-1} δ_{sc}(Si-H) loss observed by HREELS (spectra not shown).

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Thermal Effects on a Low Coverage of PH₃/Si(100)-(2x1)
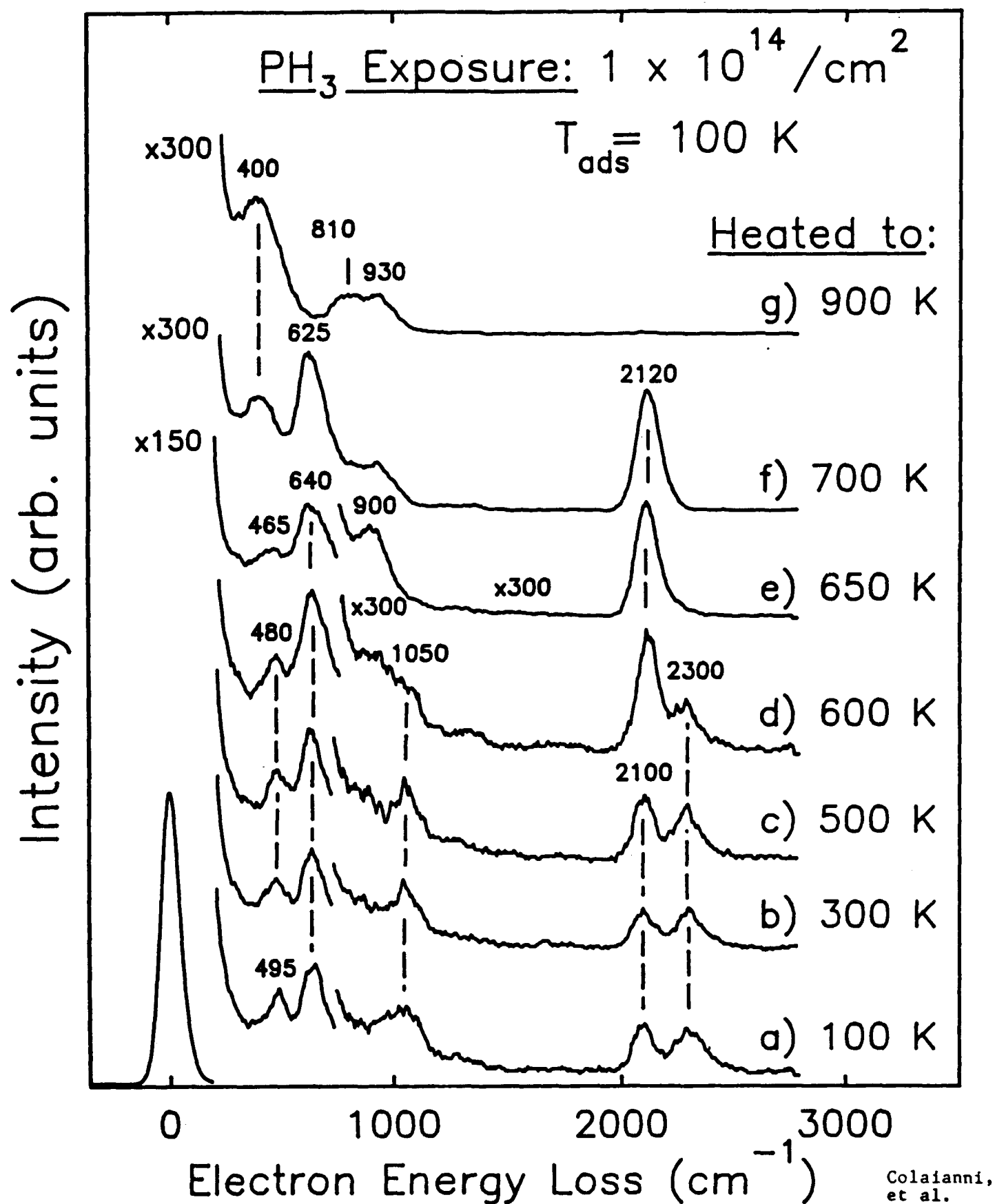
Figure 1

Thermal Desorption from Various Coverages of $PH_3/Si(100)-(2\times1)$

(A) PH_3

Mass 32 Intensity

635

485

$7.6 \times 10^{-11}A$

$\underline{PH_3}$ Exposure:

$(\times10^{14}/cm^2)$

(d) 4.0
(c) 2.0
(b) 1.0
(a) 0.5

(B) H_2

Mass 2 Intensity

770

685

$1.5 \times 10^{-8}A$

$\underline{PH_3}$ Exposure:

$(\times10^{14}/cm^2)$

(e) 13
(d) 4.0
(c) 2.0
(b) 1.0
(a) 0.5

Temperature (K)

200 400 600 800 1000 1200
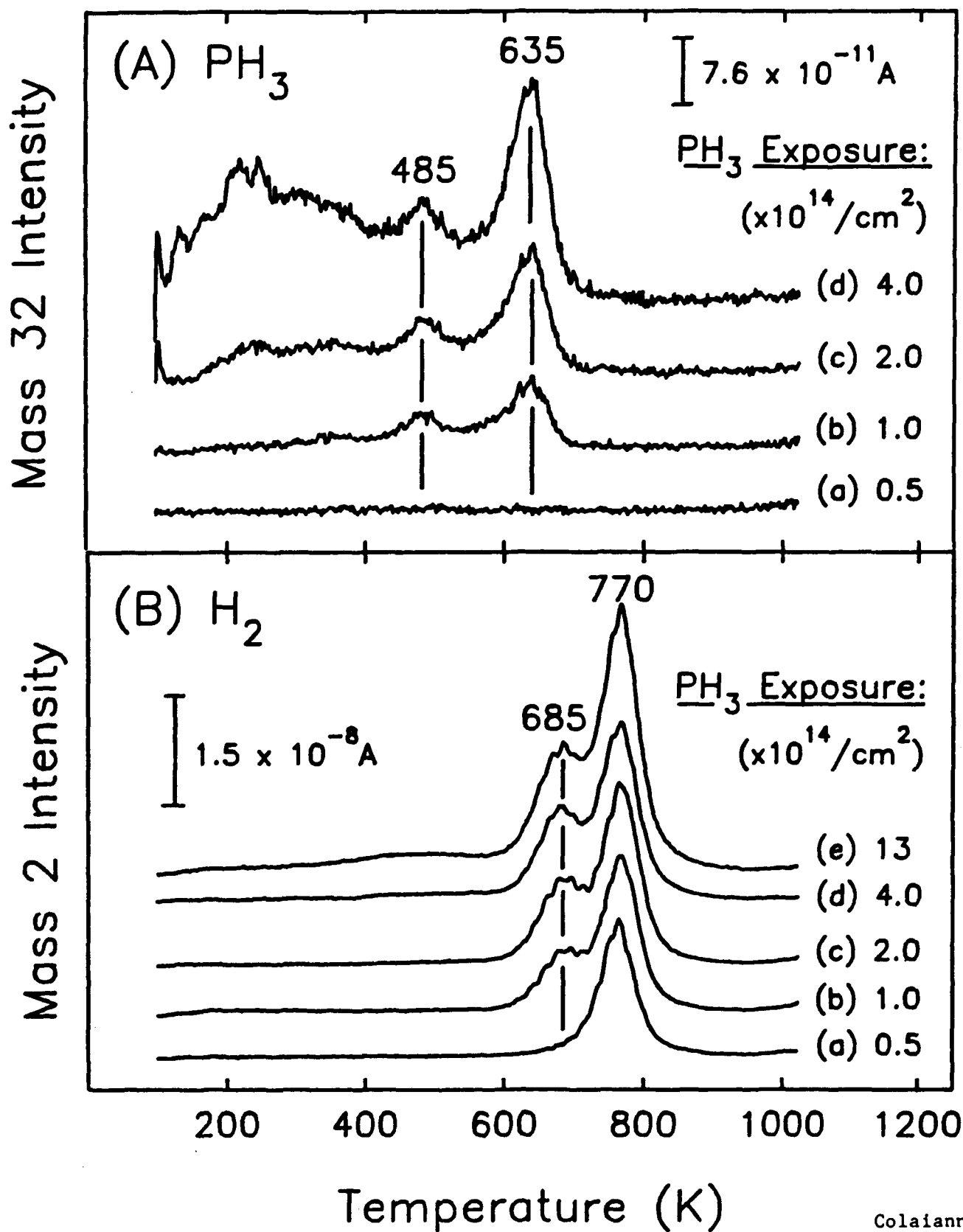
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Figure 2

H$_2$ Desorption from Clean and Phosphorus−Modified Si(100)−(2x1)

(A) PH$_3$/Si(100)−(2x1)

PH$_3$ = 1.3 × 10^{15}/cm^2

T$_{ads}$ = 100 K

770

685

10^{-8} A

(B) H·/Si(100)−(2x1)

H$_2$ = 300 L

T$_{ads}$ = 230 K

740

640

10^{-8} A

(C) H·/[PH$_3$/Si(100) → 900 K]

PH$_3$ = 2 × 10^{14}/cm^2

H$_2$ = 100 L

740

640

10^{-8} A

(D) H·/[PH$_3$/Si(100) → 900 K]

PH$_3$ = 2 × 10^{14}/cm^2

H$_2$ = 10 L

740

5 × 10^{-9} A

Intensity Mass 2

Temperature (K)
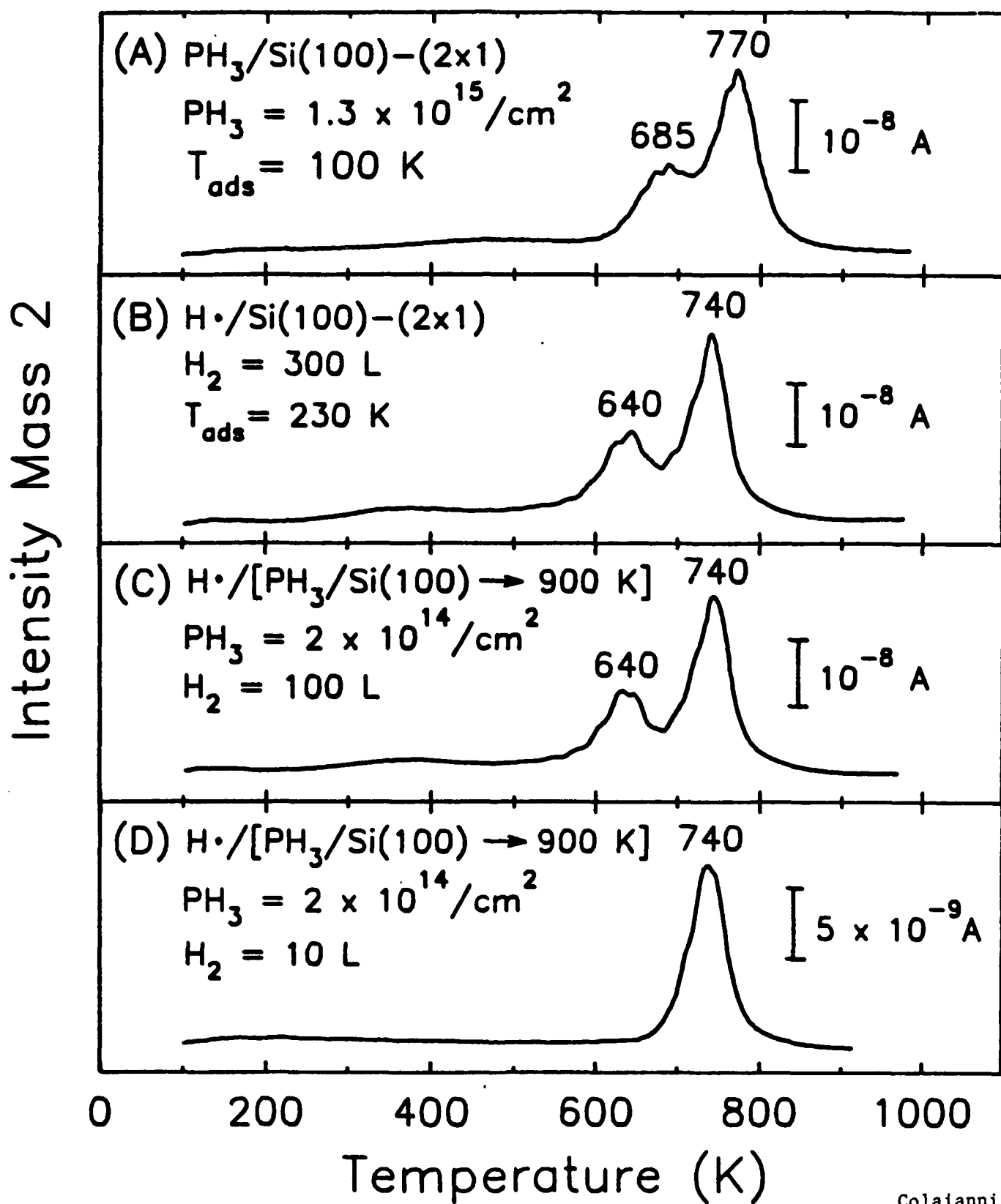
Colaianni,
et al.

Figure 3

Thermal Desorption from a
$PH_3/D \cdot /Si(100)-(2\times1)$ Interface

(a) PH_3 $PH_3 = 2.0 \times 10^{14}/cm^2$ at 100 K

$\Theta_D/\Theta_{D,sat} = 0.12$ at 230 K

Mass 32

635

10^{-11} Amps

(b) PH_2D

Mass 35

5×10^{-12} Amps

Temperature (K)
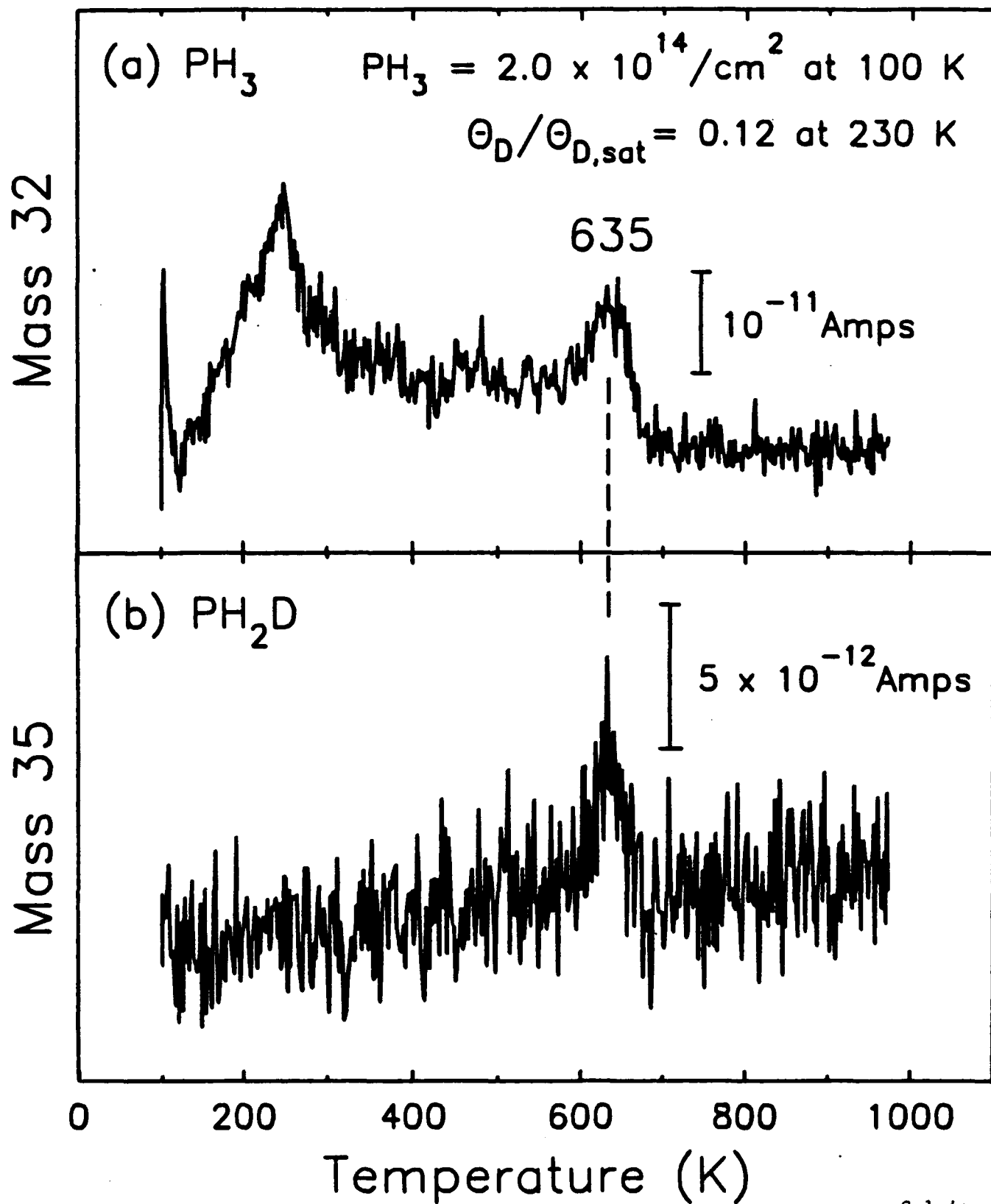
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Figure 4

Thermal Desorption of H_2, HD and D_2 from a $PH_3/D \cdot /Si(100)-(2 \times 1)$ Interface.

$PH_3(115 \text{ K})/D \cdot (575 \text{ K})/Si(100)$

$PH_3 = 6.5 \times 10^{14} \text{ cm}^{-2}$

$D_2 = 4.4$ L

(a) H_2

7.6×10^{-9} A

(b) HD

1.5×10^{-9} A

(c) D_2

7.6×10^{-11} A

Temperature (K)

Intensity (arb. units)
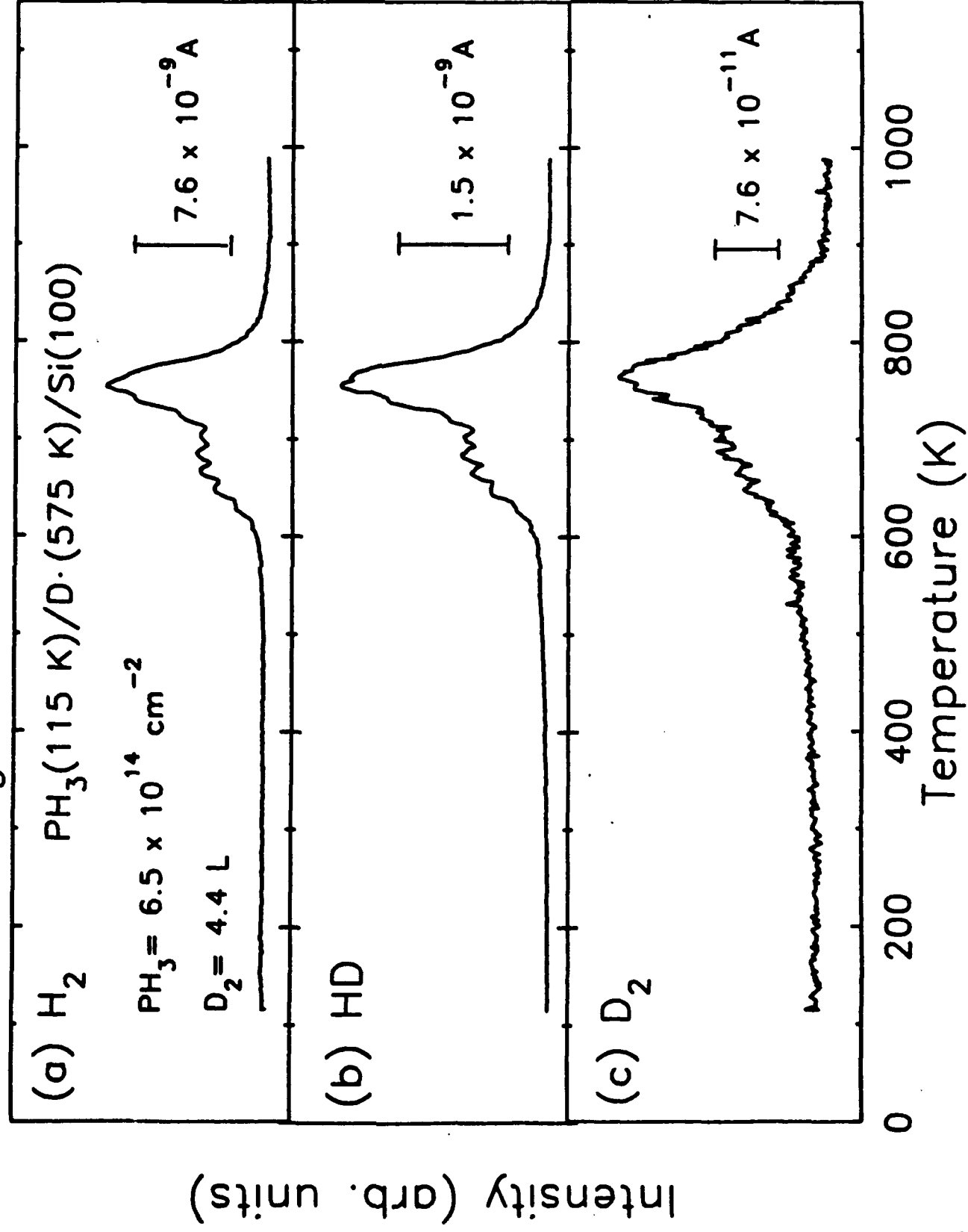
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